# <Division of Synthetic Chemistry>Structural Organic Chemistry

# Division of Synthetic Chemistry
# – Structural Organic Chemistry –

http://www.scl.kyoto-u.ac.jp/~kouzou/en/index.html

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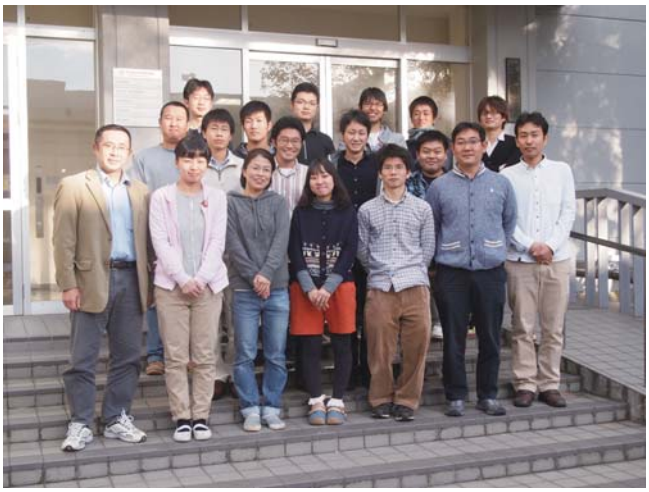
## Scope of Research

Fundamental studies are being conducted for creation of new functional π-systems with novel structures and properties, and for evaluation of their application as organic semi-conducting materials toward photovoltaic and electroluminescent devices. The major subjects are: organochemical transformation of fullerenes $C_{60}$ and $C_{70}$, specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; generation of ionic fullerene species and their application for the synthesis of functional material; synthesis of new carbon-rich materials by the use of transition metal complex; creation of new functional π-materials with unique photoelectric properties.



### KEYWORDS

π-Conjugated Systems
Endohedral Fullerenes
Functional Materials
Perovskite-based Solar Cells
Organic Solar Cells

## Selected Publications


Zhang, R.; Futagoishi, T.; Murata, M.; Wakamiya, A.; Murata, Y., Synthesis and Structure of an Open-Cage Thiafullerene $C_{69}S$: Reactivity Differences of an Open-Cage $C_{70}$ Tetraketone Relative to Its $C_{60}$ Analogue, *J. Am. Chem. Soc*., **136,** 8193-8196 (2014).

Hashikawa, Y.; Murata, M.; Wakamiya, A.; Murata, Y., Synthesis of Open-Cage Ketolactam Derivatives of Fullerene $C_{60}$ Encapsulating a Hydrogen Molecule, *Org. Lett*., **16,** 2970-2973 (2014).

Wakamiya, A.; Nishimura, H.; Fukushima, T.; Suzuki, F.; Saeki, A.; Seki, S.; Osaka, I.; Sasamori, T.; Murata, M.; Murata, Y.; Kaji, H., On-Top π-Stacking of Quasiplanar Molecules in Hole-Transporting Materials: Inducing Anisotropic Carrier Mobility in Amorphous Films, *Angew. Chem., Int. Ed*., **53,** 5800-5804 (2014).

Wakamiya, A.; Endo, M.; Sasamori, T.; Tokitoh, N.; Ogomi, Y.; Hayase, S.; Murata, Y., Reproducible Fabrication of Efficient Perovskite-based Solar Cells: X-ray Crystallographic Studies on the Formation of $CH_3NH_3PbI_3$ Layers, *Chem. Lett*., **43,** 711-713 (2014).

Chaolumen; Enno, H.; Murata, M.; Wakamiya, A.; Murata, Y., Dibenzo[*a*,*f*]perylene Bisimide: Effects of Introducing Two Fused Rings, *Chem. Asian J*., **9,** 3136-3140 (2014).

## Development of New Organic Semiconducting Materials Containing Quasiplanar Skeleton

The development of excellent charge-transporting materials with high charge carrier mobility is a crucial issue to achieve high performance in organic-device applications. In order to achieve the high charge carrier mobility using small organic molecules, it is important to control their molecular orientation in the solid state. In this work, we have designed and synthesized partially bridged triphenylamine derivatives with a quasiplanar structure. These compounds form one-dimensional on-top π-stacking aggregates in the crystalline state and showed high levels of anisotropic charge transport in the direction of the π-stacking. Furthermore, even in the vacuum deposited amorphous films, these compounds retained some of the face-on π-stacking, thus facilitating an out-of-plane carrier mobility (Figure 1). These results would provide new guideline for molecular design of organic semiconducting materials used in the amorphous state.

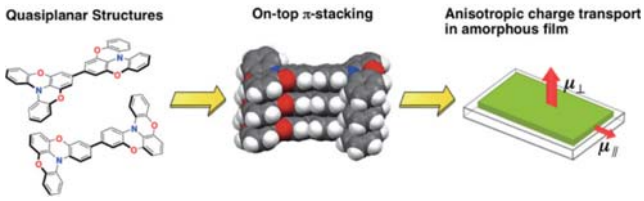



**Figure 1.** The structures of oxygen-bridged triphenylamine derivatives and their one-dimensional on-top π-stacking structure in the crystalline state. Anisotropic charge carrier mobility in the amorphous films of these compounds is also shown.

## X-Ray Crystallographic Studies on the Formation of $CH_3NH_3PbI_3$ Layers

Perovskite-based solar cells with $CH_3NH_3PbX_3$ (X= halogen) as light absorbers have attracted much attention, mostly because the perovskite layer can be easily processed in solution. Although promising PCEs of over 15% have been reported, the cells often suffer from large PCE variations, which severely hamper systematic studies on further improvements. In this work, we examined the influence of water and oxygen as well as the purity of the starting materials on the formation of the perovskite layers. Moreover, the single-crystal X-ray diffraction analyses were conducted on lead halide complexes, which potentially form during the production process. Based on these results, we have established a reproducible fabrication method for highly efficient solar cells (Figure 2).

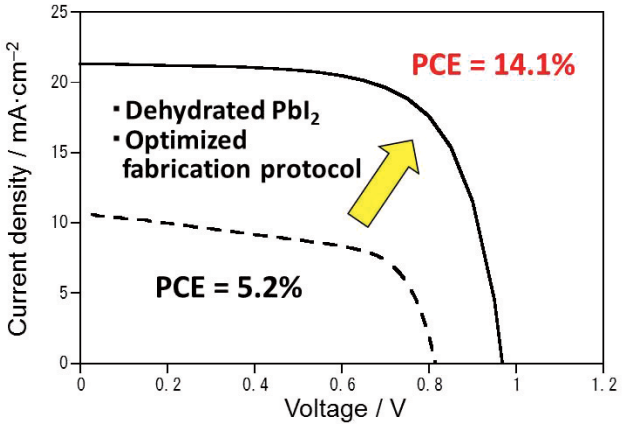



**Figure 2.** Photocurrent density-voltage curves of perovskite-based solar cell.

## Synthesis, Structure, and Properties of Dibenzo[*a*, *f*]perylene Bisimide Derivatives

Perylene bisimides (PBIs) **1** are fascinating dyes with various potential applications. In order to study the effects of introducing dibenzo-fused structure in the perylene moiety, we synthesized π-extended PBI derivative **2** with a dibenzo-fused structure at both of the *a* and *f* bonds (Figure 3). The twisted structure was characterized by X-ray crystal structure analysis. Cyclic voltammetry (CV) measurements demonstrated that two ring fusions at both sides of a naphthalene moiety, which construct a tetracene core, effectively raise the HOMO level with reference to one ring fusion at each naphthalene moiety (two anthracene cores). In particular, [*a*,*f*]-fused PBI **2** showed a broad absorption band at 735 nm with a shoulder band at 780 nm, which was markedly red-shifted by 83 nm compared to that of dibenzo[*a*,*o*]-fused PBI **3** ($\lambda_{max}$ = 697 nm).

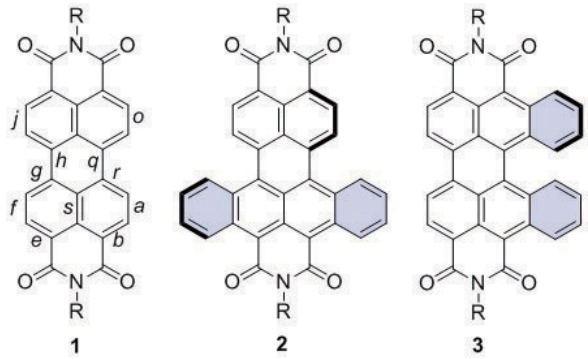



**Figure 3.** Structures of PBI **1** and dibenzo-fused PBIs **2** and **3**.